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A study of two highly active, air-stable iron (III)- μ -oxo pre-catalysts: synthetic scope of hydrophosphination using phenyl- and diphenylphosphine

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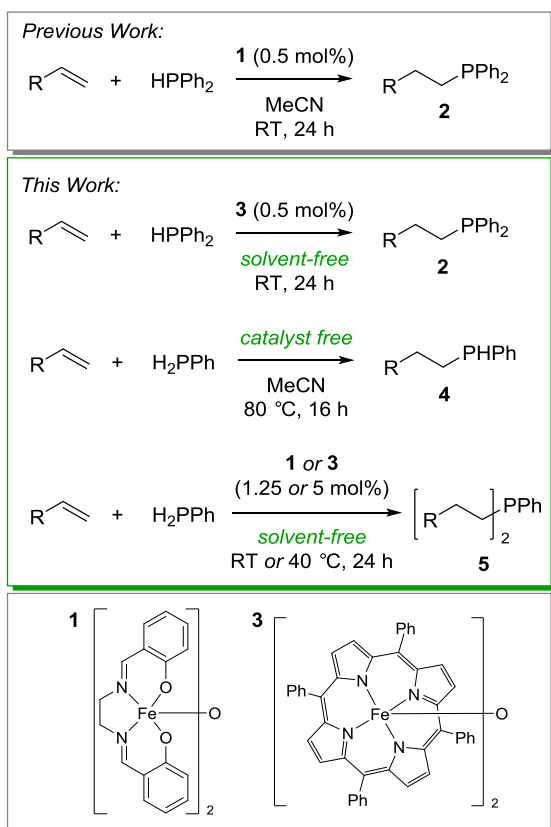
Abstract. The importance of phosphines in synthetic chemistry cannot be underestimated. Catalytic hydrophosphination offers an ideal method to prepare P–C bonds without the need for harsh reaction conditions or stoichiometric amounts of waste by-product. We herein report our studies into two biocompatible iron (III) complexes in hydrophosphination chemistry using diphenylphosphine under mild and benign reaction conditions (room temperature, solvent-free) and our extended exploration of hydrophosphination with phenylphosphine, which can be tuned to operate in the absence of catalyst under thermal conditions for single hydrophosphination or solvent-free with an iron (III) pre-catalyst to generate the products of double hydrophosphination.

Keywords: Homogeneous catalysis; Iron; Phosphines; Porphyrins; Schiff bases

Introduction

Hydrophosphination (HP),^[1] the addition of a P–H bond across an unsaturated bond, is a powerful tool in synthetic chemistry: it has the potential to be 100% atom economic, has impressive functional group tolerance in comparison to many traditional routes of P–C bond formation^[2] and gives access to vital primary, secondary or tertiary phosphines depending upon chemoselectivity and/or the phosphorus source. HP with an iron pre-catalyst is rare, with only a handful of examples reported in the literature.^[3] The attraction of iron lies in its abundance and resulting cost effectiveness: it is a sustainable, non-toxic base metal with which to develop catalysis. Seminal work in the area of iron catalyzed HP of alkenes was presented by Gaumont and co-workers^[3c] using only FeCl₂ or FeCl₃ to furnish the anti-Markovnikov product (cf. **2**, Scheme 1) or highly desirable Markovnikov products. Following this work, we reported the use of a highly active iron (III) salen- μ -oxo complex (**1**, Scheme 1) which catalyzes the HP of activated alkenes with a remarkably low catalyst loading of 0.5 mol%.^[3d] We questioned whether this reactivity is limited to **1**, or whether other N-ligands

also facilitate HP when in a metal- μ -oxo coordination environment, specifically iron (III) porphyrin complex **3**.^[4] We also wished to explore the limits of the reactivity: catalysis with complex **1** appears to be restricted to activated alkenes, but we have not explored the potential of using an activated primary phosphine in catalysis *i.e.* phenylphosphine. There are limited examples of HP with primary phosphines in the literature. Examples include Waterman's elegant and mild Zr-catalyzed route which can be tuned for single or double hydrofunctionalization products (cf. **4** and **5** respectively, Scheme 1), depending on reagent stoichiometries, and is effective for unactivated alkenes such as 1-hexene.^[5] Waterman and Wright also report tin-mediated HP which operates for styrene, 2,3-butadiene, phenyl acetylene and diphenylacetylene^[6] and finally publications from Sarazin, Carpentier and Trifonov^[7] on rare earth catalyzed HP. These latter systems operate at 70 °C or below on styrene where a 1:1 ratio of styrene:H₂PPh gives high levels of selectivity for the secondary phosphine product (cf. **4**, Scheme 1).



Scheme 1. Hydrophosphination of activated alkenes under thermal or catalytic conditions.

The desire to harness and understand the catalytic potential of iron, in particular the use of iron complexes which do not need activation is an area of interest. In the wider field of hydrofunctionalization,^[8] iron has demonstrated its wide-reaching potential across a range of transformations, not least in catalytic hydrophosphination^[3a, c] and hydrophosphonylation.^[3b, 9] In our continued efforts to develop transformations of phosphines mediated by iron, we proceeded to investigate the use of air-stable iron porphyrin-μ-oxo complex, **3**, for the HP of activated alkenes with diphenylphosphine and compare to the activity observed with **1**. We have also extended reactivity to phenylphosphine in the hydrophosphination of activated alkenes using **1** and **3**.

Results and Discussion

Reactions with HPPH₂

To initiate our study we compared the catalytic competency of complex **3** to **1** in the HP of styrene with diphenylphosphine across a range of different solvents (Table 1). Unsurprisingly, at high catalyst loading (5 mol%) both pre-catalysts are excellent at mediating this transformation. While it is difficult to argue against the biocompatible, non-toxic and easy

to handle nature of both the iron porphyrin and salen systems, the reactions remain mild: excellent spectroscopic yield (Spec. Yield) is achieved in most solvents at room temperature. It is worth noting the competency when the reaction is performed in alcohols and neat (Entries 6 and 7). We have already reported just how active **1** is at low catalyst loading and indeed, when the reaction is performed neat in the presence of 0.5 mol% **3**, the yield of **2a** remains at 96%.

Table 1. Optimization of HP reactivity in different solvents.

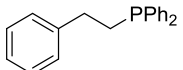
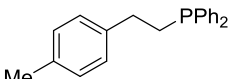
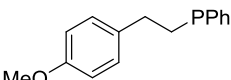
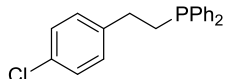
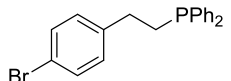
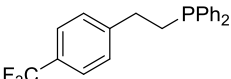
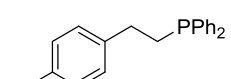
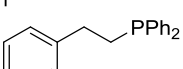

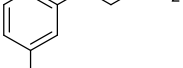
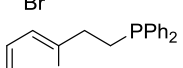
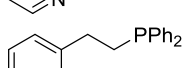
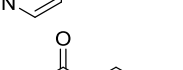
		$\text{Ph-CH=CH}_2 + \text{HPPH}_2 \xrightarrow[\text{solvent, RT, 24 h}]{\text{1 or 3 (0.5 mol\%)}} \text{Ph-CH}_2\text{-CH}_2\text{-PPh}_2 \quad \text{2a}$	
Entry	Solvent	Pre-cat: 1 2a Spec. Yield (%) ^a	Pre-cat: 3 2a Spec. Yield (%) ^a
1	toluene	76	70
2	dichloromethane	98	98
3	tetrahydrofuran	84	88
4	acetonitrile	89	84
5	pentane	-	65
6	ethanol	92 ^b	35
7	none	98	96

General reaction conditions: styrene (120 μL, 1.04 mmol, 1.82 eq), HPPH₂ (100 μL, 0.57 mmol), **1** or **3** (0.0029 mmol, 0.5 mol%), 24 h, RT, inert atmosphere. ^a) Spec. Yield = spectroscopic yield, determined by ¹H NMR spectroscopy using 1,2-DCE as a standard. ^b) Methanol used as solvent.

We then proceeded to explore the substrate scope with pre-catalyst **3** under the optimized reaction conditions. The reaction is performed solvent-free at room temperature for 24 h (Table 2). Unsurprisingly, the porphyrin complex performs competently in comparison to the simple Fe (III) salen-μ-oxo complex under similar reaction conditions, albeit in MeCN. However, interesting improvements in reactivity are seen with 4-chlorostyrene (Table 2, Entry 4) and 2- and 4-vinyl pyridine (Entries 10 and 11), where the reaction time and temperatures are reduced compared to those when **1** is employed. The improved reactivity, particularly with 2-vinylpyridine, could be attributed to the sterically congested reaction environment: the 4-coordinate porphyrin ligand surrounds the iron center and prevents competitive ligation and catalyst deactivation by the product, **2j**. Aguirre *et al.* have already demonstrated that **2j** is a good ligand for Suzuki cross-coupling,^[10] so it is possible that competitive ligation could occur at the iron center. The activity of **1** and **3** in MeCN was compared: the turnover frequency for the formation of **2a** over the initial 30 minutes is 80 h⁻¹, slowing to 55 h⁻¹ after one hour using **1** compared to 33 h⁻¹ for the first 30 minutes and only slowing marginally to 30 h⁻¹ after one hour for complex **3**. It should be

noted that for simple styrenes reactions catalyzed by **1** tend to be complete within 10 to 16 h, whereas reactions with **3** tend to need the full 24 h to go to completion. To probe reaction mechanism, the radical trap TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) was added to the HP reactions using both **1** and **3**; there is little variation in yield suggesting that catalysis is not radical mediated.

Table 2. Substrate scope for thermal hydrophosphination using HPPH₂.

Entry	Product	Pre-cat: 1 Spec. Yield ^a [Isolated yield], %	Pre-cat: 3 Spec. Yield ^b [Isolated yield], %
1	 2a	100 [89]	96 [73]
2	 2b	96 [79]	[96]
3	 2c	97 [89]	75 [71]
4	 2d	100 [74] ^c	83 [72]
5	 2e	82 [65]	85 [67]
6	 2f	85 [83]	89 [35]
7	 2g	85 [58] ^d	[85] ^a
8	 2h	100 [95]	73 [35]
9	 2i	98 [98]	[82]
10	 2j	92 [86] ^c	96 [62]
11	 2k	80 [75] ^c	75 [72]
12	 2l	80 [69]	79 [71]
13	 2m	93 [76]	99 [74]

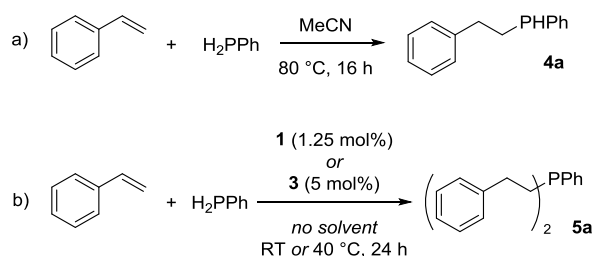
General reaction conditions: alkene (1.04 mmol, 1.82 eq), HPPH₂ (100 μ L, 0.57 mmol), **1** or **3** (0.0029 mmol, 0.5 mol%), neat or MeCN (0.35 mL), 24 h, RT, Ar. ^a) Reaction performed in MeCN (350 μ L). Spec. Yield = spectroscopic yield, determined using ¹H NMR spectroscopy with 1,2-

DCE as a standard. ^b) Reaction performed neat, spectroscopic yield determined using ¹H NMR spectroscopy with 1,2-DCE as a standard. ^c) 114 h. ^d) 60 $^{\circ}$ C. ^e) 72 h.

To prove the synthetic utility of this transformation and the benefits of using an air-stable pre-catalyst, the reaction of HPPH₂, styrene and **3** was performed in a round-bottom flask fitted with a septum under a steady stream of N₂. The reaction was scaled to use 2.3 mmol (0.4 mL) HPPH₂, 4.2 mmol (0.48 mL) styrene and 0.5 mol% (13.6 mg) **3**. Product **2a** was obtained in 85% spectroscopic yield, 63% (0.66 g) isolated yield.

Reactions with H₂PPh

Overall, the ease and scale in which **1** and **3** can be synthesized led us to investigate their ability to catalyze the reaction of phenylphosphine and styrene. We commenced this investigation by reacting phenylphosphine with styrene in the presence of iron pre-catalyst at room temperature, using a range of reaction conditions. We were somewhat surprised to find that very little reaction takes place in the presence of **1**. With 5 mol% **3** at RT, 37% of the single addition product (**4a**, SHP, where only one equivalent of styrene reacts with phenylphosphine generating the secondary phosphine) is obtained after 24 h in the absence of solvent. Extending the reaction time to 72 h increases the yield to 62%. Although a good yield, and a rare example of SHP at room temperature,^[5-7] the prolonged reaction time is somewhat limited: we decided to probe the potential for catalyst-free thermal reactivity. Undertaking the hydrophosphination procedure in the absence of catalyst, under thermal conditions, gives good conversion to the SHP product (Scheme 2a). After a short optimization process we found that a good yield of **4a** could be obtained with thermal treatment at 80 $^{\circ}$ C (61% **4a** after 18 h at 80 $^{\circ}$ C in MeCN). Addition of a further two equivalents of styrene to this reaction mixture and thermal treatment gives no further conversion, with only trace amounts of **5a** observed. Solvent is necessary for the reaction to proceed cleanly; when performed neat impurities can be seen in the ³¹P{¹H} NMR. It is interesting to note that in our hands when a 1:1 ratio of phenylphosphine:styrene is reacted in C₆D₆ at 60 $^{\circ}$ C in a J-Young NMR tube 35% of **4a** is obtained after 16 h.^[11] When the reaction is repeated in a Schlenk tube with stirring 60% **4a** is obtained. This would suggest that at temperatures of 60 $^{\circ}$ C or greater, no catalyst is necessary and thermal conditions can be used, analogous to work from Alonso and co-workers with HPPH₂.^[12]



Scheme 2. Reactivity of styrene and phenylphosphine under a) thermal and b) catalytic conditions.

Surprisingly, the thermal reaction of phenylphosphine with activated alkenes has never been reported. We decided to investigate whether this reactivity is substrate specific, but are pleased to report that a range of activated substrates undergo SHP with minimal conversion to the tertiary phosphine product under these reaction conditions (Table 3). Styrenes with functionality in the *para*-position undergo thermal SHP with only minor amounts of double addition (DHP, where two equivalents of styrene functionalize phenylphosphine furnishing a tertiary phosphine) being observed: electron-withdrawing and donating groups are tolerated, as well as styrenes with useful functionality, for example halogen-substituted styrenes (Entries 4, 5 and 8). Vinyl pyridines undergo hydrophosphination with phenylphosphine, but unfortunately the reaction appears to be less selective for the secondary phosphine product, with double hydrophosphination taking place readily: 2-vinyl pyridine undergoes HP with a 3:2 ratio of **4h**:**5h** obtained (Entry 9), 4-vinyl pyridine gives poor yield of **4i**, with multiple products observed by $^{31}\text{P}\{^1\text{H}\}$ NMR (Entry 10). Acrylates are tolerated under these reaction conditions (Entries 11 and 12).

Table 3. Substrate scope for thermal hydrophosphination using H_2PPh .

Entry	Styrene	Product	Spec. Yield ^a [Isolated yield], %
1			4a 61 [53]
2			4b 44 [40]
3			4c 82 [70]
4			4d 76 [66]
5			4e 93 [78]
6			4f 60 [55]
7			4g 79 [76]

8			4h 76 [61] (34) ^b
9			4i 60 (40) ^b
10			4j 35 [31]
11			4k 81 [64]
12			4l 74 [72]

General reaction conditions: styrene (0.285 mmol, 1 eq), phenylphosphine (63 μL , 0.57 mmol, 2 eq), MeCN (200 μL), 16 h, 80 $^\circ\text{C}$, Ar. ^a Spec. Yield = spectroscopic yield, determined by ^1H NMR spectroscopy using THF as a standard. ^b Product of double hydrophosphination observed, spectroscopic yield shown in brackets.

Purification of the SHP products, even in the presence of DHP side-products, is trivial: the reaction mixture is subjected to vacuum to remove any unreacted H_2PPh and volatile styrenes, then use of short path distillation apparatus or cold finger at reduced pressure with gentle heating to 60 $^\circ\text{C}$ allows distillation of products **4a** to **4k** away from any traces of DHP product or unreacted, non-volatile, styrenes. Unfortunately no reaction is observed with unactivated substrates; substrates primed for nucleophilic attack must be used, for example, allyl benzene and 1-hexene give only trace amounts of product. Similarly, the transformation with cyclohexylphosphine fails to deliver an appreciable amount of product.

We then proceeded to investigate whether we could integrate thermal and catalytic HP. We anticipate that the electronic nature of phosphine products **4a** to **4k** is similar to that of diphenylphosphine and should thus be able to undergo iron catalyzed HP in the presence **1** or **3**. By changing the reaction stoichiometries, the product of double hydrophosphination is observed (Scheme 2b). Using **1**, no reaction is obtained using DHP conditions at room temperature and heating to 40 $^\circ\text{C}$ is needed (Table 4). We envisage that this reaction proceeds *via* thermal SHP and on formation of small amounts of SHP product it is immediately transferred to an iron catalyzed HP cycle where it can undergo DHP, thus helping to drive forward the thermal process. Alternatively, it is possible to undertake thermal SHP at 80 $^\circ\text{C}$ to afford secondary phosphines of the form **4**, followed by addition of catalyst and further reaction at RT to generate products of the form **5**. Using the one pot procedure, 1.25 mol% **1** and heating to 40 $^\circ\text{C}$, we observe clean formation of the DHP product, with only small quantities of unreacted SHP product

(<15%) and unreacted starting materials. In some Fe-catalyzed HP reactions small quantities of side product are observed in the ^{31}P NMR.^[13] These are believed to be products of Michael addition,^[14] where styrene starting material undergoes further attack by the HP product. This may hint at a potential reaction mechanism which proceeds *via* a zwitterionic intermediate. The reaction proceeds best neat, presumably the increased concentration results in more favorable DHP. However, in an effort to use milder reaction conditions, when the catalyst loading is increased the reaction does not proceed cleanly and mixtures of products start to form. On the other hand **3** is an excellent pre-catalyst for DHP at RT and, unlike **1**, side-products are not obtained at the higher catalyst loading of 5 mol%.

Table 4. Substrate scope for catalytic double hydrophosphination.

		$\text{R}-\text{CH}=\text{CH}_2 + \text{H}_2\text{PPh} \xrightarrow[\text{3 (5 mol\%)}]{\text{1 (1.25 mol\%)}} \text{R}-\text{CH}(\text{PPh})_2$ 40 °C, 24 h or RT, 24 h			
Entry	Product	Pre-cat: 1 Spec. Yield, ^a %	Pre-cat: 3 Spec. Yield ^a [Isolated yield], %		
1		5a	66	81 [79]	
2		5b	30	63 [62]	
3		5c	78	74 [70]	
4		5d	60	96 [89]	
5		5e	58	[71]	
6		5f	36	92 [88]	

General reaction conditions: styrene (2.28 mmol, 4 eq), phenylphosphine (63 μL , 0.57 mmol, 1 eq), **1** (1.25 mol%) or **3** (5 mol%), neat, 24 h, 40 °C or RT, Ar. ^a) Spec. Yield = spectroscopic yield, determined by ^1H NMR spectroscopy using 1,2-DCE as a standard.

The phosphine products are oils at room temperature, however, the structure of phosphine **5a** was confirmed by ligation to iron, which is achieved in

good yield (65% **Fe-5a**) by stirring two equivalents of the ligand with $\text{FeCl}_2 \cdot \text{THF}_{1.5}$ at room temperature in dry THF (Figure 1). Precipitation of the iron complex is observed within minutes and can be isolated by removal of solvent by filtration followed by washing with cold pentane. The iron complex is obtained as a distorted tetrahedral complex with bond lengths of 2.433(1) and 2.415(1) Å, for Fe–P1 and Fe–P2 respectively and 2.232(1) and 2.238(1) for Fe–Cl1 and Fe–Cl2 respectively.

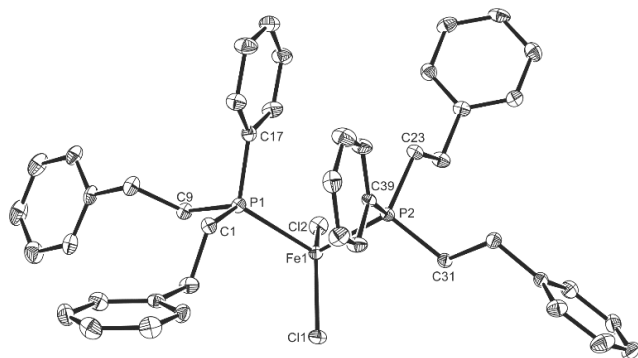
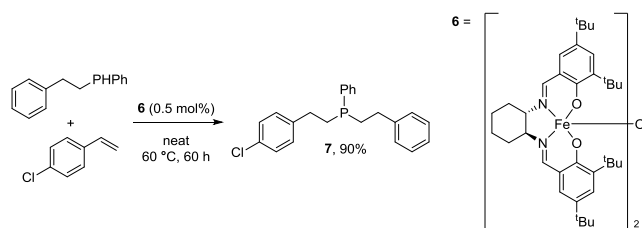


Figure 1. X-ray crystal structure of complex **Fe-5a** (hydrogen atoms omitted for clarity and ellipsoids represented at 30% probability). Selected bond lengths (Å) Fe1–Cl1 2.232(1); Fe1–Cl2 2.238(1); Fe1–P1 2.433(1); Fe1–P2 2.415(1); P1–C1 1.827(4); P1–C9 1.830(4); P1–C17 1.815(4); P2–C23 1.822(4); P2–C31 1.835(4); P2–C39 1.818(4); C1–C2 1.533(6); C9–C10 1.540(5); C23–C24 1.536(5); C31–C32 1.528(5). Selected bond angles (°): Cl2–Fe1–Cl1 127.30(4); Cl2–Fe1–P1 102.55(4); Cl1–Fe1–P2 100.41(4); Cl2–Fe1–P2 111.64(4); Cl1–Fe1–P1 111.04(4); P2–Fe1–P1 101.25(4).

With easy access to chiral salen complexes we then questioned whether we could afford optically active tertiary phosphines using our methodology. By first applying thermal conditions to generate the SHP product, **4a**, we should then be able to use a chiral iron pre-catalyst to install a second alkyl substituent stereoselectively. P-stereogenic phosphines have found extensive use in metal mediated asymmetric catalysis,^[1a, 15] notably in early leading research from Knowles into asymmetric hydrogenations.^[16] Although excellent examples of transition metal catalyzed enantioselective HP exist,^[15a-d, 17] this would be an unusual example of iron mediating an enantioselective HP reaction, with the other leading literature examples being stoichiometric studies^[18] or of intermolecular hydrophosphonylation.^[3b] We initiated our investigations by preparing the Jacobsen's ligand motif and ligating to Fe to form the corresponding μ -oxo complex, **6**.^[19] When **4a** is reacted in the presence of two equivalents 4-chlorostyrene, 0.5 mol% **6** at 60 °C for 60 h 90% **7** is obtained (Scheme 3). Unfortunately no enantioinduction is obtained with pre-catalyst **6** which was determined by oxidation of the isolated

phosphine, **7**, with two equivalents of H₂O₂ and extraction of the phosphine oxide into CH₂Cl₂ to give a stable product that can be studied using chiral separation techniques. It is worth noting that for product **7** Kagan's amide^[20] and a selection of lanthanide shift reagents (Eu(FOD)₃ and Eu(hfc)₃) do not give peak separation by both ¹H and ³¹P{¹H} NMR. Instead, circular dichroism was used to demonstrate that enantioinduction has not taken place. This could be due to rapid P-inversion at the Fe-center,^[21] particularly at the raised reaction temperature, and/or due to lack of stereocontrol induced by the metal complex. It is nonetheless a useful method to make unsymmetrically substituted tertiary phosphines.



Scheme 3. Product of unsymmetrical HP.

Conclusion

In summary, we have demonstrated that an iron (III) porphyrin complex can catalyze the hydrophosphination of activated alkenes with diphenylphosphine. The transformation operates under environmentally benign conditions (solvent-free, room temperature) with a low loading of a simple air-stable base-metal catalyst. In general, this porphyrin catalyst appears to be as active over as wide a range of alkene substrates as our original iron (III) salen complex. We have also presented two new methods to functionalize activated alkenes with phenylphosphine; a thermal route which selectively forms the secondary phosphine products and an iron (III) salen catalyzed route which can furnish symmetrical tertiary phosphines in one pot or a two-step method which can be used to synthesize unsymmetrically substituted tertiary phosphines. It is clear that iron pre-catalyst **6** is not able to induce enantioselective hydrophosphination and therefore further development is needed in this area in order to achieve this goal.

Experimental Section

General method for hydrophosphination using HPPH₂ and pre-catalyst **3**

Carried out under an argon atmosphere in an M-Braun glove box. **3** (0.5 mol%) was weighed out into a Schlenk tube. Styrene (1.04 mmol, 1.86 eq) was added followed by diphenylphosphine (100 μ L, 0.57 mmol, 1 eq). After stirring at room temperature for 24 h, the Schlenk tube was placed under vacuum and the excess starting styrene and solvent removed. For spectroscopic yields reaction solutions were exposed to air and filtered through a silica

gel plug using CH₂Cl₂. Solvent was removed by blowing nitrogen over the oil before addition of 1,2-dichloroethane as an integration standard. CDCl₃ was used as the NMR solvent. All products obtained have been previously reported and characterised,^[3d] NMR spectra for isolated products is provided.^[13]

General method for thermal single hydrophosphination

The reaction was prepared under an argon atmosphere in an M-Braun glove box. Styrene (0.285 mmol, 1 eq) was placed in a Schlenk tube, acetonitrile (200 μ L) and phenylphosphine (63 μ L, 0.57 mmol, 2 eq) were added. After stirring at 80 °C for 16 h, the Schlenk tube was placed under vacuum and the excess starting styrene and solvent removed leaving a colorless oil. A spectroscopic yield was obtained under an atmosphere of argon prior to the sample being purified by short-path distillation under reduced pressure (2×10^{-2} mbar, 60 °C).

General method for catalytic double hydrophosphination

The reaction was prepared under an argon atmosphere in an M-Braun glove box. **1** (4.7 mg, 1.25 mol%) was weighed out into a Schlenk tube. Styrene (2.28 mmol, 4 eq) was added to this followed by and phenylphosphine (63 μ L, 0.57 mmol, 1 eq). After stirring at 40 °C for 24 h, the Schlenk tube was placed under vacuum and the excess starting styrene removed. A spectroscopic yield was obtained prior to purification by column chromatography (1% EtOAc/petroleum ether).

General method for catalytic unsymmetrical double hydrophosphination

The reaction was prepared under an argon atmosphere in an M-Braun glove box. **6** (0.5 mol%) was weighed out into a Schlenk tube. CH₃CN (200 μ L) was added to this followed by **4a** (0.5 mmol, 1 eq) and a substituted styrene (1 mmol, 2 eq) was added. After stirring at 60 °C for 60 h, the Schlenk tube was placed under vacuum and the excess starting styrene and solvent removed. A spectroscopic yield was obtained prior to purification by column chromatography (1% EtOAc/petroleum ether).

Characterization Data

Table 3, Entry 1, **4a**

Colourless oil (32 mg, 53%). ¹H NMR (500 MHz, 298 K, C₆D₆) δ 7.34 (s, 2H), 7.13 - 7.07 (m, 6H), 6.94 - 6.93 (m, 2H), 4.09 (dm, 1H, J = 210 Hz), 2.61 - 2.56 (m, 2H), 1.93 - 1.84 (m, 2H); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃) δ 142.1, 139.7, 135.7 (d, J = 4.8 Hz), 133.6 (d, J = 1.9 Hz), 128.3 (d, J = 4.8 Hz), 128.1, 127.9, 125.9, 34.5 (d, J = 2.9 Hz), 25.2 (d, J = 3.8 Hz); ³¹P{¹H} NMR (202 MHz, 298 K, CDCl₃) δ -52.3; IR (solid) ν 2912, 2283, 1602, 1495, 1434, 740, 720, 692 cm⁻¹; HRMS (EI) 213.0828 (calcd.), 213.0834 (obs.).

Table 3, Entry 2, **4b**

Colourless oil (26 mg, 40%). ¹H NMR (500 MHz, 298 K, C₆D₆) δ 7.36 - 7.33 (m, 2H), 7.07 - 7.04 (m, 3H), 6.95 (d, 2H, J = 7.9 Hz), 6.88 (d, 2H, J = 7.9 Hz), 4.10 (dm, 1H, J = 206.3 Hz), 2.67 - 2.53 (m, 2H), 2.12 (s, 3H), 1.90 - 1.80 (m, 2H); ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃) δ 139.1 (d, J = 7.3 Hz), 135.8 (d, J = 12.3 Hz), 133.5 (d, J = 15.5 Hz), 129.1, 129.0, 128.3 (d, J = 5.6 Hz), 128.1, 128.0, 34.0 (d, J = 8.1 Hz), 25.3 (d, J = 13.5 Hz), 20.7; ³¹P{¹H} NMR (202 MHz, 298 K, CDCl₃) δ -53.0; IR (solid) ν 2920, 2283, 1591, 1515, 1436, 807, 740 cm⁻¹; HRMS (EI) 227.0984 (calcd.), 227.0987 (obs.).

Table 3, Entry 3, **4c**

Colourless oil (40 mg, 70%). ¹H NMR (500 MHz, 298 K, C₆D₆) δ 7.40 - 7.32 (m, 2H), 7.09 - 7.00 (m, 3H), 6.88 (d, 2H, J = 10 Hz), 6.76 (d, 2H, J = 10 Hz), 4.12 (dm, 1 H, J =

206.3 Hz), 3.33 (s, 3H), 2.65 - 2.56 (m, 2H), 1.98 - 1.86 (m, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -52.8; IR (solid) ν cm^{-1} 2930, 2283, 1610, 1511, 1434, 820, 741, 695; HRMS (EI) 243.0933 (calcd.), 243.0936 (obs.).

Table 3, Entry 4, 4d

Colourless oil (47 mg, 66%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.34 - 7.32 (m, 2H), 7.10 - 7.08 (m, 3H), 7.06 (d, 2H, J = 8.3 Hz), 6.58 (d, 2H, J = 8.3 Hz), 4.05 (ddd, 1H, J = 206.4, 7.8, 5.9 Hz), 2.46 - 2.35 (m, 2H), 1.80 - 1.66 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, C_6D_6) δ 139.8 (d, J = 7.6 Hz), 134.7 (d, J = 12.4 Hz), 132.9 (d, J = 16.2 Hz), 131.1, 128.9, 127.7, 127.5, 127.3, 33.0 (d, J = 8.6 Hz), 24.2 (d, J = 14.3 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -53.0; IR (solid) ν 2923, 2285, 1490, 1434, 734, 695 cm^{-1} ; HRMS (EI) 265.0544 (calcd.), 265.0548 (obs.).

Table 3, Entry 5, 4e

Colourless oil (65 mg, 78%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.34 - 7.30 (m, 2H), 7.20 (d, 2H, J = 8.3 Hz), 7.08 - 7.07 (m, 3H), 6.51 (d, 2H, J = 8.3 Hz), 4.03 (ddd, 1H, J = 206.4, 7.3, 5.9 Hz), 2.41 - 2.32 (m, 2H), 1.81 - 1.64 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, C_6D_6) δ 133.5 (d, J = 15.6 Hz), 131.3, 129.8, 128.3 (d, J = 5.7 Hz), 128.2, 128.1, 128.0, 127.9, 33.6 (d, J = 8.3 Hz), 24.8 (d, J = 13.7 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -52.7; IR (solid) ν 2924, 2283, 1586, 1487, 1434, 801, 741, 695 cm^{-1} ; HRMS (EI) 291.1297 (calcd.), 291.1304 (obs.).

Table 3, Entry 6, 4f

Colourless oil (44 mg, 55%). ^1H NMR (400 MHz, 298 K, C_6D_6) δ 7.43 - 7.39 (m, 1H), 7.31 - 7.25 (m, 4H), 7.08 - 7.05 (m, 2H), 6.74 - 6.72 (m, 1H), 6.65 - 6.63 (m, 1H), 4.00 (d, 1H, J = 205.8 Hz), 2.43 - 2.37 (m, 2H), 1.74 - 1.62 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K, C_6D_6) δ 135.8, 134.3 (d, J = 15.6 Hz), 133.3 (d, J = 19.5 Hz), 130.0, 129.2, 129.1, 128.9, 125.9, 34.8 (d, J = 8.1 Hz), 25.3 (d, J = 14.5 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 298 K, C_6D_6) δ -52.6; IR (solid) ν 3073, 2310, 1550, 1479, 1366, 759, 655 cm^{-1} .

Table 3, Entry 7, 4g

Colourless oil (61 mg, 76%). ^1H NMR (400 MHz, 298 K, C_6D_6) δ 7.55 - 7.51 (m, 1H), 7.50 - 7.47 (m, 2H), 7.43 - 7.34 (m, 4H), 7.23 - 7.19 (m, 2H), 7.09 - 7.03 (m, 3H), 6.97 - 6.95 (m, 2H), 4.11 (ddd, 1H, J = 207.4, 7.6, 6.4 Hz), 2.72 - 2.57 (m, 2H), 1.97 - 1.85 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K, C_6D_6) δ 141.8 (d, J = 11.3 Hz), 141.2, 139.1 (d, J = 2.2 Hz), 133.6 (d, J = 15.5 Hz), 128.7, 128.6, 127.2, 127.1, 127.0, 127.0, 126.9, 34.1 (d, J = 8.2 Hz), 25.1 (d, J = 13.7 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 298 K, C_6D_6) δ -52.7; IR (solid) ν 3065, 2284, 1602, 1432, 820, 747, 695 cm^{-1} ; HRMS (EI) 291.1304 (calcd.), 291.1297 (obs.).

Table 3, Entry 8, 4h

Colourless oil (52 mg, 61%). ^1H NMR (400 MHz, 298 K, C_6D_6) δ 7.28 - 7.26 (m, 2H), 7.15 (m, 2H, partially obscured by solvent), 7.08 - 7.04 (m, 3H), 6.69 - 6.65 (m, 1H), 6.60 - 6.59 (m, 1H), 3.98 (dm, 1H, J = 206.5 Hz), 2.38 - 2.29 (m, 2H), 1.74 - 1.57 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, C_6D_6 , C-P not observed) δ 133.5 (d, J = 15.3 Hz), 131.2, 129.8, 129.7, 129.0, 128.4 (d, J = 5.6 Hz), 128.0, 126.6, 122.5, 33.9 (d, J = 8.6 Hz), 24.6 (d, J = 14.0 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 298 K, CDCl_3) δ -52.6; IR (solid) ν 2923, 2283, 1593, 1567, 1475, 1434, 882, 781, 741, 694 cm^{-1} ; HRMS (EI) 293.0089 (calcd.), 293.0095 (obs.).

Table 3, Entry 9, 4i

Colourless oil. ^1H NMR (500 MHz, 298 K, C_6D_6) δ 8.54 - 8.53 (m, 1H), 7.59 - 7.57 (m, 1H), 7.54 - 7.51 (m, 2H), 7.34 - 7.32 (m, 3H), 7.12 - 7.10 (m, 2H), 4.18 (ddd, 1H, J = 211.0, 7.9, 6.3 Hz), 2.98 - 2.91 (m, 2H), 2.31 - 2.22 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 161.4 (d, J = 7.8 Hz), 149.3, 136.3, 133.6 (d, J = 15.4 Hz), 128.5, 128.4, 128.2, 122.7, 121.2, 36.8 (d, J = 7.5 Hz), 23.2 (d, J = 12.5 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ

-51.7; IR (solid) ν 2913, 2279, 1590, 1474, 1433, 811, 741 cm^{-1} ; HRMS (EI) 216.0937 (calcd.), 216.0939 (obs.).

Table 3, Entry 10, 4j

Colourless oil (19 mg, 31%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 8.51 - 8.50 (m, 2H), 7.32 - 7.29 (m, 2H), 7.09 - 7.07 (m, 3H), 6.51 - 6.50 (m, 2H), 4.00 (ddd, 1H, J = 206.9, 7.8, 5.9 Hz), 2.36 - 2.25 (m, 2H), 1.73 - 1.62 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 150.0, 133.5 (d, J = 15.6 Hz), 128.4 (d, J = 5.7 Hz), 128.2, 128.1 (d, J = 8.6 Hz), 127.9, 123.2, 33.4 (d, J = 7.6 Hz), 23.7 (d, J = 14.3 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -52.5; HRMS (EI) 232.0886 (calcd.), 232.0889 (obs.).

Table 3, Entry 11, 4k

Colourless oil (36 mg, 64%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.34 - 7.29 (m, 2H), 7.03 (m, 3H), 4.02 (d, 1H, J = 207.4 Hz), 3.28 (s, 3H), 2.18 - 2.17 (m, 2H), 1.88 - 1.86 (m, 2H); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -51.2; IR (solid) ν 2923, 2280, 1593, 1568, 1475, 1434 cm^{-1} ; HRMS (EI) 181.0413 (calcd.), 181.0414 (obs.).

Table 3, Entry 12, 4l

Colourless oil (49 mg, 72%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.32 - 7.29 (m, 2H), 7.03 - 7.02 (m, 3H), 4.06 (ddd, 1H, J = 207.9, 8.3, 5.9 Hz), 3.95 - 3.92 (m, 2H), 2.28 - 2.19 (m, 2H), 2.00 - 1.89 (m, 2H), 1.38 - 1.32 (m, 2H), 1.18 - 1.12 (m, 2H), 0.76 - 0.73 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3 , carbonyl carbon not observed) δ 134.4, 129.1 (d, J = 5.7 Hz), 128.8 (d, J = 18.1 Hz), 128.7, 64.6, 33.5 (d, J = 8.6), 31.3, 19.7, 19.3, 19.2, 14.1; $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -51.2; IR (solid) ν 2958, 2873, 2285, 1730, 1600, 1464, 1435, 1388, 803, 737 cm^{-1} ; HRMS (EI) 291.1303 (calcd.), 291.1297 (obs.).

Table 4, Entry 1, 5a

Colourless oil (144 mg, 79%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.50 - 7.48 (m, 2H), 7.20 - 7.18 (m, 6H), 7.14 - 7.04 (m, 3H), 7.00 - 6.99 (m, 4H), 2.67 - 2.54 (m, 4H), 1.93 - 1.81 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 142.8 (d, J = 11.6 Hz), 138.0 (d, J = 14.9 Hz), 132.6 (d, J = 18.9 Hz), 129.1, 128.6, 128.5, 128.2, 126.0, 32.3 (d, J = 15.3 Hz), 30.3 (d, J = 12.9 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, CDCl_3) δ -23.4; HRMS (EI) 319.1610 (calcd.), 319.1614 (obs.). Unknown side-products observed in reaction catalyzed by 1.

Table 4, Entry 2, 5b

Colourless oil (134 mg, 62%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.66 - 7.63 (m, 2H), 7.47 - 7.42 (m, 3H), 7.13 (d, 4H, J = 8.6 Hz), 6.88 (d, 4H, J = 8.6 Hz), 3.82 (s, 6H), 2.75 - 2.64 (m, 4H), 2.13 - 2.01 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 157.9, 134.9 (d, J = 11.7 Hz), 132.6 (d, J = 18.8 Hz), 129.3 (d, J = 6.3 Hz), 129.1, 129.0, 128.5 (d, J = 7.0), 113.9, 55.3, 31.4 (d, J = 15.3 Hz), 30.6 (d, J = 12.9 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -24.4; IR (solid) ν 2931, 1610, 1583, 1509, 1463, 1434, 817, 742, 696 cm^{-1} ; HRMS (EI) 379.1821 (calcd.), 379.1826 (obs.).

Table 4, Entry 3, 5c

Colourless oil (138 mg, 63%). ^1H NMR (300 MHz, 298 K, C_6D_6) δ 7.53 - 7.52 (m, 2H), 7.27 - 7.25 (m, 3H), 7.17 (d, 4H, J = 8.3 Hz), 6.74 (d, 4H, J = 8.3 Hz), 2.54 - 2.46 (m, 4H), 1.84 - 1.74 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 142.8 (d, J = 11.6 Hz), 132.5 (d, J = 18.9 Hz), 129.0, 128.6, 128.5, 128.4, 128.1, 126.0, 32.2 (d, J = 15.3 Hz), 30.3 (d, J = 12.9 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, CDCl_3) δ -24.6. Unknown side-products observed in reaction catalyzed by 1.

Table 4, Entry 4, 5d

Colourless oil (217 mg, 80%). ^1H NMR (500 MHz, 298 K, C_6D_6) δ 7.49 - 7.47 (m, 2H), 7.34 - 7.30 (m, 7H), 6.95 - 6.93 (m, 4H), 2.60 - 2.48 (m, 4H), 1.99 - 1.86 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 141.4 (d, J = 11.3 Hz), 137.3 (d, J = 14.5 Hz), 132.5 (d, J = 19.2 Hz), 131.4, 129.8, 129.2, 128.5 (d, J = 7.2 Hz), 119.7, 31.6 (d, J

= 15.7 Hz), 30.2 (d, J = 13.2 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, C_6D_6) δ -24.2.

Table 4, Entry 5, 5e

Colourless oil (224 mg, 82%). ^1H NMR (400 MHz, 298 K, C_6D_6) δ 7.36 (m_{br}, 2H), 7.16 - 7.15 (m, 3H, partially obscured by solvent), 7.13 - 7.12 (m, 4H, partially obscured by solvent), 6.73 - 6.64 (m, 4H), 2.39 - 2.32 (m, 4H), 1.67 - 1.55 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 298 K, CDCl_3) δ 144.9 (d, J = 11.5 Hz), 132.7, 132.5, 131.2, 130.0, 129.3, 129.2, 128.7 (d, J = 7.3 Hz), 126.9, 122.5, 32.0 (d, J = 16.0 Hz), 30.1 (d, J = 13.3 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 298 K, CDCl_3) δ -23.5. Unknown side-products observed in reaction catalyzed by **1**.

Table 4, Entry 6, 5f

Colourless oil (161 mg, 88%). ^1H NMR (400 MHz, 298 K, CDCl_3) δ 8.56 - 8.55 (m, 2H), 7.66 - 7.58 (m, 4H), 7.42 - 7.40 (m, 3H), 7.15 - 7.12 (m, 4H), 2.96 - 2.89 (m, 4H), 2.27 - 2.23 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, CDCl_3) δ 161.9, 149.2, 136.5, 132.6 (d, J = 19.1 Hz), 129.0, 128.5, 128.4, 122.6, 121.1, 34.5 (d, J = 16.2 Hz), 28.0 (d, J = 12.4 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 298 K, CDCl_3) δ -22.9; HRMS (EI) 336.1392 (calcd.), 336.1395 (obs.).

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